$\theta=55°$ and $\lambda=0.1$, where the strongest absorption spectra were obtained. The value of λ obtained corresponds to a quadrupole interaction $eqQ=(7.5\pm1.5)\times10^{-8}$ ev for the tetrahedral site and $eqQ=(9.0\pm1.8)\times10^{-8}$ ev for the octahedral site. A better value of eqQ could be obtained above the Curie temperature (272°C) where the splitting of the $I=\frac{3}{2}$ state would be purely quadrupolar.

ACKNOWLEDGMENTS

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Magnetic Susceptibility of Cerous Magnesium Nitrate

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The most striking features of the behavior of cerous magnesium nitrate at liquid helium temperatures—extremely anisotropic susceptibility with $g_{\parallel}\approx0$, a large temperature-independent term in $\chi_{\perp}$, the spin-lattice relaxation time varying as the twelfth or higher power of T in the region of 2°K—have until very recently received no detailed explanation. A measurement of $\chi_{\perp}$ between 4° and 300°K was undertaken to elicit information on the energies of the excited doublets within the $J=\frac{5}{2}$ ground multiplet, and thus to provide a guide for the reassessment of the crystal field parameters. We find δ_1 and δ_2 to be 30 and (roughly) 200 cm^{-1}, respectively, in contrast to the 113 and 150 cm^{-1} of existing theory. The results are at variance with the published data for $\chi_{\perp}$ above 85°K, but are in fairly good agreement with the recent findings of Leask and Wolf at low temperatures.

I. INTRODUCTION

THE salt cerous magnesium nitrate (CMN), $Ce_2Mg_3(NO_3)_{12}\cdot24H_2O$, exhibits interesting and unusual features in its behavior at low temperatures. Its paramagnetism arises from the Ce^{3+} ion. Its $^2F_{\frac{5}{2}}$ ground state is split by the crystalline electric field into three Kramers doublets characterized roughly by $J_Z=\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$.[1] In the liquid-helium region, the salt obeys the Curie law very accurately, the two highest doublets being essentially unoccupied; the effective spin is $\frac{1}{2}$ and the g factor is extremely anisotropic[2]: $g_{\parallel}\lesssim0.05$,[3,4] and $g_{\perp}\approx1.84$.[2] The interactions which cause deviations from Curie's law at very low temperatures are extremely small and their effect upon the susceptibility does not become significant until 0.01°K or lower.[4,5] This feature and the concomitant one of very small specific heat below 1°K have already been made use of quite extensively in low temperature thermometric and magnetic cooling applications.[6] Finally, the spin-lattice relaxation time τ is strongly temperature dependent in the liquid helium region,[2] and in the customary Casimir-DuPré type of investigation one finds that τ increases from immeasurably small ($<10^{-4}$ sec) to immeasurably large ($>10^{-2}$ sec) in lowering the temperature from 2.2° to 1.7°K. This type of behavior was confirmed by us in a series of relaxation-time measurements[4,7] undertaken mainly to derive an independent estimate of the magnetic contribution to the specific heat as a check upon adiabatic demagnetization data.

To improve the understanding of the behavior of CMN and, in particular, to seek information on the splittings in the ground state, we decided to study the departures from Curie law behavior which set in at higher temperatures as the populations of the excited levels become significant. While this work was in progress, we learned that Wolf and collaborators were

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[7] R. P. Hudson and R. S. Kaeser (to be published).

independently engaged upon a similar program and had, in fact, identified the first excited state as $J_Z=\pm\frac{3}{2}$ and placed it at approximately 25 cm^{-1} above the ground doublet. Subsequently, these workers have shown[8,9] that a consistent picture may be developed to explain both the temperature dependence of τ between 1.7°K and 2.2°K and the $\chi_\perp$ vs T behavior between 10°K and 20°K, based upon such a location for the $J_Z=\pm\frac{3}{2}$ level; confirmatory data are supplied by specific heat measurements[10] and by the relaxation-time measurements in this laboratory.[7] The investigations reported here covered the temperature region 4°–300°K and lead to estimates of the splittings for both excited doublets, δ_1 and δ_2.

II. EXPERIMENTAL PROCEDURE

The susceptibility of a small (6.0 mg) single crystal of CMN was measured by a modified Faraday method in an apparatus[11] following the design of Senftle and colleagues.[12] A small hole was drilled in the center of, and perpendicular to, a plane face of the crystal (i.e., along the c axis) to accommodate a quartz fiber suspension 40 μ diam. The "perpendicular susceptibility" $\chi_\perp$ was measured.

The apparatus was originally designed for the measurement of very weak (semiconductor) susceptibilities. The elastic constant of the quartz spiral was calibrated by means of a standard paramagnetic specimen in the same magnetic field as was used for the actual measurement. Since CMN has a susceptibility ranging from 10–500 times larger than susceptibilities usually measured by the apparatus, the measuring field was reduced accordingly. As a result, it became apparent that it would be most satisfactory to calibrate the apparatus by normalizing the data to the known value of $g_\perp$ in the low-temperature region. Initially, we adopted the value[13] 1.838 for $g_\perp$; and we also made a second computation with the value 1.832, as found directly by Leask and Wolf[9] in their measurements in the helium-hydrogen region.

After determining the susceptibility at 4.2°K, the temperature was allowed to rise: first, by slowly reducing the thermal contact between the sample chamber and the liquid helium; and second, by allowing the liquid helium to boil off. During the first stage, the pressure of the transfer gas in the annular space surrounding the sample chamber was reduced in steps. Between steps, the rate of heating was allowed to reach a steady value to permit a measurement. At pressures below about 25 μ Hg, the heat transfer no longer depends appreciably on pressure and the second stage must be commenced. The rise from 4.2°K to room temperature required about 7 hr. During the entire measurement, the inner (sample) chamber contained helium gas at a pressure of 10 mm Hg. The temperature was measured at the wall of the inner chamber (at about 4 mm from the crystal) by means of a silver-gold vs gold-cobalt thermocouple.

The accuracy of the measured value of temperature thus depends upon the quality of the thermometer calibration, the smallness of the heat leaks from the surroundings to both the thermometer and the specimen via their respective suspensions, and the efficiency of the gas in the sample chamber in maintaining equality of temperature between the thermometer and the specimen. Hence, a very slow rate of rise of temperature is required for a reliable measurement of T; this condition is furthest from realization in the region immediately above 4.2°K, as is shown by the point at "4.7°K" (Fig. 1) which was evidently at 5.1°K in reality. It is interesting that the error on this particular point is in the direction opposite to that normally experienced in the low-temperature region (see Discussion).

III. THEORETICAL

The theory of the Ce^{3+} ion in a field of C_{3v} symmetry as developed by Judd[14] can account moderately well for the g values in the ground doublet by a suitable choice of the parameters in the crystal field potential and by taking into account the mixing of the $^2F_{7/2}$ states into the basic $^2F_{5/2}$ multiplet. It is, however, inadequate to explain the large temperature-independent term in the low-temperature susceptibility,[2] still less the over-all behavior of $\chi_\perp$ between 4° and 300°K.

Using the parameters given by Judd, one derives[15] for the "perpendicular susceptibility"

$$\chi_\perp=\frac{N\beta^2}{4kZ}\left[\left(\frac{1.835^2}{T}+0.10\right)+\left(\frac{0.001^2}{T}+0.06\right)e^{-162/T}\right.$$
$$\left.+\left(\frac{0.551^2}{T}-0.16\right)e^{-216/T}+\cdots\right]\cdots. \quad (1)$$

Here, $\chi_\perp/N$ is the susceptibility per Ce^{3+} ion, β is the Bohr magneton, k is the Boltzmann constant, and Z is a normalizing factor, $\sum_i \exp(-\delta_i/kT)$, to take into account the distribution over the various levels. Four terms multiplied by Boltzmann factors appropriate to the $J=\frac{7}{2}$ levels which are effectively zero at room temperature and below (the energies of these levels are 2000–3000 cm^{-1}) are omitted from this expression.

At liquid helium temperatures, the above expression

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[15] We are indebted to J. C. Eisenstein for the derivation of this formula.

reduces to

$$\chi_\perp = N\beta^2/4k[(1.835^2/T)+0.10]. \tag{2}$$

It will be observed that Judd's choice of parameters gives the correct value for $g_\perp$ (the fit to $g_\parallel$ is much less satisfactory) but the second term, representing temperature-independent paramagnetism, is less than half that found experimentally.[2] Moreover, the first excited doublet, $J_z = \pm\frac{3}{2}$, lies at 35–40 deg (see above) rather than the 162 deg appearing in Eq. (1).

To interpret our $\chi_\perp$ vs T data we make use of the generalized form of Eq. (1),

$$\chi_\perp = (N\beta^2/4kZ)\{[(g_1^2/T)+B'+E']+[(0/T)+C'-B']\exp[-\delta_1/T]+[(g_3^2/T)-C'-E']\exp[-\delta_2/T]\} \tag{3}$$

$$= \frac{[(A/T)+B+E]+(C-B)\exp[-\delta_1/T]+[(D/T)-C-E]\exp[-\delta_2/T]}{1+\exp(-\delta_1/T)+\exp(-\delta_2/T)}. \tag{3a}$$

The value for $(B+E)$ can be found from the data for the lowest temperatures where the susceptibility obeys the relation $\chi_\perp = A/T+(B+E)$. The best value for δ_1 is specified quite stringently by the course of $\chi_\perp$ vs T in the range 10°–40°K. If δ_2 is so large that its effect is negligible in this region (the data are consistent with such a picture, in fact up to 60°K), we may write

$$\chi_\perp(T<40°\mathrm{K}) = \frac{[(A/T)+B+E]+(C-B)\exp(-\delta_1/T)}{1+\exp(-\delta_1/T)}, \tag{4}$$

whence one derives

$$\Delta\chi \exp(\delta_1/T) - \chi_\perp = (B-C), \tag{4a}$$

where $\Delta\chi = \chi_0 - \chi_\perp$ and $\chi_0 = A/T+(B+E)$. By fitting the data to Eq. (4a), the value of δ_1 may be fixed to the nearest degree and the value of $(B-C)$ is obtained simultaneously. Now knowing $(B-C)$ and $(B+E)$, we obtain $(C+E)$ immediately.

For the value of g_3, only an educated guess may be made: If one neglects the influence of the $J=\frac{7}{2}$ states, then one finds $g_3 = (18/7)\sin^2\theta$, and $g_1 = (18/7)\cos^2\theta$, where θ is a parameter specifying the mixture of the basic J_z states in the wave functions.[14] For $g_1 = 1.84$, $\theta = 32°$ and $g_3 = 0.73$. Alternatively, Eq. (1) (which is known to have serious shortcomings) gives $g_3 = 0.55$. Fortunately, in the region of temperature where the δ_2 terms of Eq. (3) together contribute significantly to the magnitude of $\chi_\perp(T>60°\mathrm{K})$, D/T will be small if $g_3 \sim 1$, and a quite large uncertainty in g_3 will be of minor importance.

We now rearrange Eq. (3a) into the form

$$\exp(\delta_2/T) = [\chi_\perp - (D/T)+C+E] \times[\Delta\chi - (B-C+\chi_\perp)\exp(-\delta_1/T)]^{-1}, \tag{3b}$$

and plot the logarithm of the right-hand side against T^{-1} to derive δ_2.

A correction for the diamagnetism was applied, using data quoted by Mookherji.[16] The contribution amounts to 1% at 25°K, 3.7% at 100°K, and 10% at 300°K, so that the expected uncertainty in this correction will not materially affect the interpretation of our results.

IV. RESULTS

The paramagnetic susceptibility is presented as a plot of $\chi_\perp$ vs $1/T$ in Figs. 1 and 2. As explained in Sec. II, we converted our relative susceptibility measurements into absolute values by demanding that the slope of $\chi_\perp$ vs $1/T$ at the lowest temperatures corresponded to the known value of $g_\perp$ (i.e., g_1). The points of Figs. 1 and 2 have been normalized to $g_\perp = 1.832$, as found by Leask and Wolf.[8] In cgs units per gram we find

$$\chi_0 = [(411.4/T)+29.3]\times 10^{-6}.$$

Leask and Wolf obtain 28.85 for the constant term, with no diamagnetic correction. When this is applied (+0.37), our figure of 29.3 is to be compared with their 29.22. Thus by forcing our $\chi_\perp$ vs $1/T$ *slope* to fit theirs (or the known g value), the actual *values* of $\chi_\perp$ come into excellent agreement in the liquid helium region. If we normalize our data to $g_\perp = 1.838$,[13] the constant term is changed to 29.5.

The data of Leask and Wolf, summarized by a curve, are included in Fig. 1. Their actual points were obtained

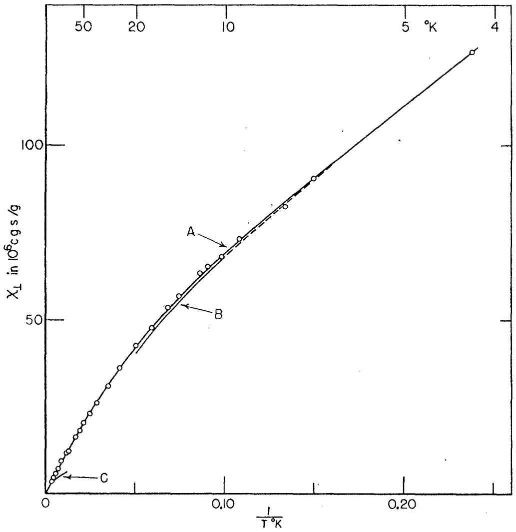

FIG. 1. "Perpendicular susceptibility," $\chi_\perp$, for CMN against reciprocal of absolute temperature: curve A and circles, this research; curve B, data of Leask and Wolf[9] (interpolation between 10°K and 4°K); curve C, data of Mookherji.[16]

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[16] A. Mookherji, Indian J. Phys. 23, 410 (1949).

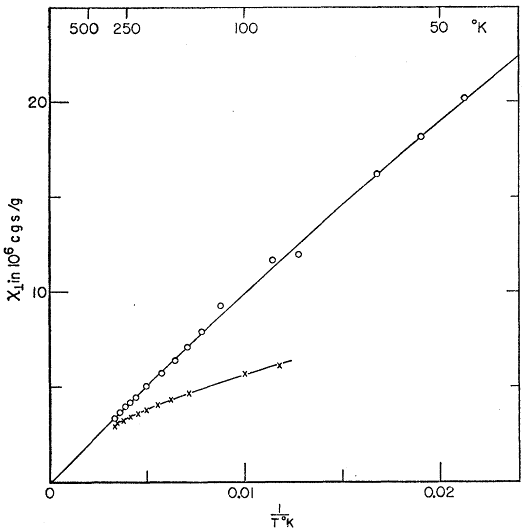

FIG. 2. $\chi_\perp$ against $1/T$ in the high-temperature region: o, this research; ×, data of Mookherji.[16]

below 4.2°K and in the range 10°–20°K. As may be observed, the two sets of data diverge in the latter region. Though the actual separation is small, it never-the less leads to a substantial difference between the values for δ_1 derived by them (38.4 deg) and by us (43 deg).

Analyzing the complete data as described in Sec. III, we find $\delta_2 = 300 \pm 50$ deg, $(B+E) = 29.27$, $(B-C) = 25.0$, and hence $(C+E) = 4.3$. The curves through the experimental points in Figs. 1 and 2 were computed using these values together with $A = 411.4$, $D = 65.3$, and $\delta_1 = 43$ deg. Also shown in both figures are the results obtained by Mookherji.[16] Apart from the immediate neighborhood of room temperature, the disagreement is very pronounced.

V. DISCUSSION

As already mentioned, the observed variation of $\chi_\perp$ with T indicates that the crystal field parameters used in previous applications of the theory are incorrect. Unfortunately, it is not a simple matter to adjust these parameters and produce a better accord with the susceptibility while maintaining the correct g values.[17] A systematic search for the right parameters is being conducted in a machine calculation program.

At low temperatures our data are in quite good numerical agreement with those of Leask and Wolf, but the differences are still sufficient to lead us to the figure of 43 deg for δ_1, while they obtain 38 deg. The latter figure seems to be preferable on the sum of the various experimental findings,[7–10] yet the discrepancy seems to be outside experimental error. Undoubtedly our greatest source of error lies in the thermometry, and experience has shown[11] that the true temperature of the salt will be less than that indicated by the thermocouple, a difference which is in the direction of the observed divergence. But we believe that it is unlikely that our temperatures, above 10°K at least, are in error by more than 0.25°K; and, moreover, that the accuracy should improve with rising temperature. Yet the divergence is observed to increase as T rises from 10° to 20°K. Under our conditions of measurement, we should not expect difficulties arising from the anisotropy of the salt, such as one might encounter in using the same apparatus to measure the much smaller $g_\parallel$. It is not impossible that the differences are real, the properties of CMN varying from specimen to specimen.

The uncertainty in δ_2 ($\pm 16\%$) is large because the scatter in the data is magnified in such an analysis as that of Eq. (3b). Measurements of $\chi_\parallel$ at high temperatures would be very valuable for providing additional information on δ_2. Such data exist but are probably erroneous (see below). A calculation of the matrix elements involved in Eq. (3a), using the approximate wave functions referred to in Sec. III together with our derived values for the splittings, gives surprisingly good agreement with the observed values viz., $B = 29.4$, $C = 4.0$, and $E = 1.1$. In view of our neglect of admixtures from the $J = 7/2$ levels, this agreement must be regarded for the present as somewhat fortuitous.

Mookherji[16] has studied both $\chi_\perp$ and $\chi_\parallel$ over the range 85°–300°K Starting at the latter temperature with values some 15% larger, our $\chi_\perp$ diverges rapidly from his until they differ by a factor two at 85°K. The curve through Mookherji's points shows no evidence of turning upwards at the low-temperature extreme toward the by-now-well-established course of $\chi_\perp$ with $1/T$ below 20°K.

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For valuable advice on the theoretical aspects of this work we are indebted to J. C. Eisenstein, and to R. Orbach and W. P. Wolf, who also kindly made available to us details of their measurements in advance of publication.

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[17] J. C. Eisenstein (private communication).